

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C11D 3/50, 17/00	A1	(11) International Publication Number: WO 92/18601 (43) International Publication Date: 29 October 1992 (29.10.92)
(21) International Application Number: PCT/US92/03156 (22) International Filing Date: 16 April 1992 (16.04.92) (30) Priority data: 686,209 16 April 1991 (16.04.91) US (71) Applicants: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). THE PROCTER AND GAMBLE COMPANY [US/US]; Miami Valley Laboratories, Post Office Box 398707, Cincinnati, OH 45239-8707 (US). (72) Inventors: MERZ, Russell, J. ; Post Office Box 398707, Cincinnati, OH 45239-8707 (US). NORBURY, Robert, J. ; BUTTERY, Howard, J. ; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). MICHAEL, William, R. ; Post Office Box 398707, Cincinnati, OH 45239-8707 (US).		(74) Agents: BJORKMAN, Dale, A. et al.; Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: IMPROVEMENTS IN COATED PERFUME PARTICLES (57) Abstract Perfume particles comprise perfume dispersed within certain water-insoluble nonpolymeric carrier materials and encapsulated in a protective shell by coating with a friable coating material. The coated particles allow for preservation and protection of perfumes which are susceptible to degradation or loss in storage and in cleaning compositions. Such perfume particles exhibit improved performance when they incorporate a modifier material according to this invention. In use, the surface coating fractures and the underlying carrier/perfume particles efficiently deliver a large variety of perfume types of fabrics or other surfaces.		

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	RU	Russian Federation
CG	Congo	KP	Democratic People's Republic of Korea	SD	Sudan
CH	Switzerland	KR	Republic of Korea	SE	Sweden
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
DE	Germany	MC	Monaco	TC	Togo
DK	Denmark			US	United States of America

- 1 -

5 IMPROVEMENTS IN COATED PERFUME PARTICLES

TECHNICAL FIELD

 The present invention relates to improvements
in perfume particles which comprise perfume dispersed
10 within a solid carrier material and encapsulated with a
friable coating. Such coated particles provide perfume
delivery systems in, for example, cleaning and fabric
conditioning compositions. The incorporation of certain
modifiers in the particles substantially enhances
15 perfume-delivery performance on wet, and especially on
dry, fabrics in a laundering context.

BACKGROUND OF THE INVENTION

 This invention is based on the concept of
20 controlled perfume release, i.e., perfume release at a
time and under conditions that will achieve the desired
perfume effect. In general, this is a very old idea,
and various methods for achieving this end have been
developed, from the simple idea of putting perfume in
25 wax candles to the complex technology of
microencapsulation.

 One aspect of the concept of controlled
release of perfume is providing slow release of perfume
over an extended period of time. This is generally
30 achieved by blending perfume with a substance that will,
in essence, "trap" the perfume so that small amounts of
perfume are released over time. The use of high
molecular weight polymeric substances having perfume
incorporated therein to provide controlled release of
35 perfume over time is known. See, for example, U.S.
Patent 4,184,099 Lindaner et al, issued January 15,
1980; European Patent Application 0 028 118, Leonard,

- 2 -

published May 6, 1981; and U.S. Patent 4,110,261, Newland, issued August 29, 1978, which teach combining perfume with a release controlling medium and forming the combination into a solid product for air freshening.

5 Textile laundering is also concerned with controlled release of perfumes. Application of this concept allows for slowing down or preventing release of perfume through long periods of shelf storage. Such a concept also allows for using much lower levels of
10 perfume in product since much less perfume is wasted.

 In another aspect of perfume delivery technology, perfume/carrier systems are designed to provide long-lasting perfumery benefits to fabrics in a laundering system. Indeed, it is this aspect of perfume
15 delivery that the present invention primarily addresses.

 Co-pending U.S. Patent Applications 350,434, filed May 11, 1989; 482,441, filed February 20, 1990; and 656,116, filed February 14, 1991 (with U.S. Patent 4,973,422, issued November 27, 1990) all relate to
20 various perfume/solid core/coating particles which are designed to deliver perfume to surfaces, especially in fabric laundering or fabric softening compositions.

 It is the primary objective of this invention to optimize the performance of perfume/solid
25 core/coating particles, especially on wet and dry fabrics, as well as to minimize batch-to-batch variability in their performance.

BACKGROUND ART

30 Perfume preservation over storage times can be achieved in a variety of ways. The perfume can be made a part of the package for the composition. The perfume can be combined with plastic used to make a bottle, or the perfume can be mixed with a polymer substance and
35 the product used to coat a cardboard package composition, as is disclosed in U.S. Patent 4,540,721,

- 3 -

Staller, issued September 10, 1985. Either way, the perfume is released over time from the polymer matrix.

The perfume/controlled release agent may also be in the form of particles mixed into the laundry composition. One method taught to achieve this end is combining the perfume with a water-soluble polymer, forming into particles and adding to a laundry composition, as is described in U.S. Patent 4,209,417, Whyte, issued June 24, 1980; U.S. Patent 4,339,356, Whyte, issued July 13, 1982; and U.S. Patent 3,576,760, Gould et al, issued April 27, 1971.

The perfume may also be adsorbed onto a porous carrier material, which may be a polymeric material. See, for example, U.K. Patent Publication 2,066,839, Bares et al (applied for in the name of Vysoka Skola Chemicko Technologika), published July 15, 1981. These methods may also be used to mask unpleasant odors in a composition or to protect perfume from degradation by harsh components in a laundry composition. Such methods will provide these benefits only for dry powder or granular type compositions because, as soon as the polymer is hydrated the perfume is released. Thus, these methods provide for perfume fragrance benefits upon opening of the product package and loading into the washing apparatus. While these benefits are desirable, it would be even more desirable to have a method which allows for delivery of undiluted, undissipated and unaltered perfume to fabric and release of the perfume at the end of the laundry process so that the fabric is scented with the desirable perfume odor.

Of course, one method for achieving this end is putting the perfume into a product which goes directly into the dryer. This way, the perfume is delivered to the fabric in the dryer cycle. Such a method is taught in both U.S. Patent 4,511,495, Melville, issued April 16, 1985, and U.S. Patent

- 4 -

4,636,330, Melville, issued January 13, 1987. Both
teach forming perfume into particles with a carrier.
These particles are then formulated into a composition
which is applied to textiles prior to putting into the
5 dryer or prior to clothes-line drying.

An even more desirable method for delivering
perfume to laundered fabric would be one which provides
for protection of the perfume through the washing
process and hence delivery of the perfume to fabric in
10 essentially its original state.

Such a method must allow for prevention of
dilution, degradation or loss of the perfume during the
wash cycle of the laundry process. This is done by
utilizing a system that releases the perfume in the
15 drying process or later after the perfume has been
delivered to the fabric. Preventing release of perfume
during the washing process involves very different and
more difficult technology. Such protection must be
stable in not only the heat-elevated conditions of the
20 wash but must also be stable against degradation by
water and other harsh chemicals in the washing process
such as bleach, enzymes, surfactants, etc.

One method which has been developed to provide
these benefits is perfume microencapsulation. Here the
25 perfume comprises a capsule core which is coated
completely with a material which maybe polymeric. U.S.
Patent 4,145,184, Brain et al, issued March 20, 1979,
and U.S. Patent 4,234,627, Schilling, issued November
18, 1980, teach using a tough coating material which
30 essentially prohibits the diffusion out of the perfume.
The perfume is delivered to fabric via the microcapsules
and is then released by rupture of the microcapsules
such as would occur with manipulation of the fabric.

Another method of perfume delivery involves
35 providing protection of perfume through the wash cycle,
with release of perfume in the heat-elevated conditions

- 5 -

of the dryer. U.S. Patent 4,096,072, Brock et al, issued June 20, 1978, teaches a method for delivering fabric conditioning agents to textiles through the wash and dry cycle via particles containing hydrogenated
5 castor oil and a fatty quaternary ammonium salt. Perfume may be incorporated into these particles. However, it is not clear whether the perfume thus incorporated is released in the wash cycle or carried in the particles to the dryer and released there, as the
10 particles soften.

U.S. Patent 4,402,856, Schnoring et al, issued September 6, 1983, teaches a microencapsulation technique which involves the formulation of a shell
15 material which will allow for diffusion of perfume out of the capsule only at certain temperatures. This allows for maintenance of the perfume particles through storage and additionally through the wash cycle. The particles adhere to the fabric and are carried over to the dryer. Diffusion of the perfume out of the capsules
20 then occurs only in heat-elevated conditions of the dryer. These particles are made of gelatin, an anionic polymer and a hardening agent.

U.S. Patent 4,152,272, Young, issued May 1, 1979, teaches incorporating perfume into waxy particles
25 to protect the perfume through storage in dry compositions and through the laundry process. The perfume then diffuses through the wax matrix of the particles on the fabric in the heat-elevated conditions of the dryer.

30 It is desirable to provide compositions comprising perfume particles that can be incorporated in liquid as well as dry granular or powder compositions and provide long-term storage stability.

It is desirable to provide a method for
35 delivering a broad range of perfume materials to fabric

- 6 -

or other surfaces during a cleaning or fabric- or fiber-conditioning process.

It is desirable to provide perfumed particles which are stable in fluid compositions, but which
5 liberate their perfume, in use.

It would be most desirable to have a perfumed cleaning or conditioning composition which provides improved product odor, improved odor of perfume released during the cleaning process, and improved odor and
10 intensity of perfume delivered to the surface being cleaned. It is of particular importance to provide improved perfume release on both wet and dry fabrics, after a laundering operation.

15 SUMMARY OF THE INVENTION

The invention encompasses an improved method for preparing a particulate perfume delivery system comprising a solid core material bearing a perfume material and having a friable coating surrounding said
20 perfume-bearing core material, comprising the steps of combining said core with said perfume and encapsulating said perfumed core with a friable polymeric coating, said improvement comprising introducing a modifier material into said perfume delivery system.

25 A preferred and convenient method herein is wherein said modifier material is introduced as a component of said perfume material. Preferred modifiers herein include phthalate-type materials, especially diethyl phthalate. Preferred perfume materials herein
30 are substantially free of dipropylene glycol. Preferred friable coatings are aminoplast polymers, especially the reaction product of an amine selected from urea and melamine, or mixtures thereof, and the aldehyde is selected from formaldehyde, acetaldehyde,
35 glutaraldehyde, or mixtures thereof. Highly preferred

- 7 -

coatings are aminoplast polymers which comprise ureaformaldehyde polymer.

5 An alternate method herein is where said modifier material is introduced as a component of said core material. Again, the modifier material is preferably of the phthalate-type, especially diethyl phthalate.

10 In yet another, but less convenient, method, said modifier material is introduced as a component of the friable coating material.

The invention also encompasses perfume delivery systems, comprising: coated perfume particles having an average size, when coated, of less than about 350 microns which comprise from about 5% to about 50% by weight of a perfume dispersed in from about 50% to about 15 95% by weight of a nonpolymeric solid fatty alcohol or fatty ester carrier material, or mixtures thereof, said alcohols or esters having a molecular weight of from about 100 to about 500 and a melting point of from about 20 37°C to about 80°C, said alcohols or esters being substantially water-insoluble, said particles having a substantially water-insoluble friable coating on their outer surfaces, said particles containing at least about 0.05% by weight of a modifier. Such particles 25 preferably have an average size not greater than 150 microns. As noted above, said modifier material is preferably of the phthalate-type, especially diethyl phthalate, and the perfume material is preferably substantially free of dipropylene glycol. The friable 30 coating on the particles is preferably an aminoplast resin, such as there action product of an amine selected from urea and melamine, and an aldehyde selected from formaldehyde, acetaldehyde and glutaraldehyde, and mixtures of said amines and said aldehydes. The carrier 35 material is preferably selected from the C₁₄-C₁₈ alcohols, especially myristyl alcohol. (As will be

- 8 -

disclosed hereinafter, other solid core carrier materials can also be used herein, including certain polymeric materials.) The particles are preferably those wherein said modifier material is introduced as a component of said perfume material.

The invention also encompasses detergent compositions, especially fabric laundry detergents, comprising one or more deterative surfactants, optionally, one or more builders, and a perfume delivery system comprising perfume particles which comprise from about 5% to about 50% by weight of a perfume dispersed in from about 50% to about 95% by weight of a nonpolymeric solid fatty alcohol or fatty ester carrier material, or mixtures thereof, said alcohols or esters having a molecular weight of from about 100 to about 500 and a melting point of from about 37°C to about 80°C, said alcohols or esters being substantially water-insoluble, said particles having a substantially water-insoluble friable coating on their outer surfaces, said coated particles having an average size less than about 350 microns, said particles containing at least about 0.05% by weight of a modifier. Said particles are prepared as noted above.

The invention also encompasses fabric softener compositions, as well as other consumer products wherein prolonged perfume delivery is desired, as will be disclosed hereinafter.

All percentages, ratios and proportions herein are by weight, unless otherwise specified.

DETAILED DESCRIPTION OF THE INVENTION

Apart from being especially effective in providing their intended benefit of prolonged perfume release, the coated perfumed particles of the present invention are designed to provide several important advantages over the various encapsulated perfumes of the

- 9 -

art. First, the preferred coatings used herein are stable not only in solid or granular laundering compositions, but also in liquid compositions. Second, the coated perfumed particles herein do not require any additional treatment, such as the application of additional cationic coatings, to achieve the desired result of substantivity to fibers and fabrics. Third, using solid carrier materials as the "cores" of the particles herein makes the particles less fragile than perfume particles having liquid cores. This not only simplifies manufacture, but also means that the particles are more robust under storage and shipping conditions in laundering and other types of compositions. The nonpolymeric carrier materials used herein have the additional advantage over many polymeric perfume carriers in that they are degradable in the environment or in sewage treatment facilities and/or that they are available from renewable resources such as plant and animal fats and oils. Moreover, the particles herein allow for the formulation of condensed detergent granules with desirable perfume levels, but without the undesirably high odor levels in the product package that would be associated with the use of raw perfume.

However, in order to achieve the above-described benefits and yet function in the intended manner as a perfume delivery vehicle, it is important that the perfume-carrying materials employed herein be carefully selected from among the various classes of prospective perfume carrier materials broadly disclosed in the art. Preferably, the carrier is somewhat polar so that it will imbibe a considerable amount of a wide variety of perfume ingredients. (As noted hereinafter, certain nonpolar, polymeric carriers are also useful herein, albeit not as preferred as the nonpolymeric polar carriers.) Fatty alcohols and esters meet this requirement, but fatty acids tend to be too polar to

- 10 -

imbibe the desired high levels of many perfume ingredients. The carrier should be solid at room temperature so that stable particles can be produced and stored, yet must be somewhat softenable, in-use, to help release the perfume. Again, fatty alcohols and esters meet these requirements. Moreover, the carriers should be substantially water-insoluble (as defined more fully hereinafter) under usage conditions. Fatty alcohols and esters also meet these requirements. It is also important that the core material be selected to be "compatible" with the material used to make the friable coating. This is especially important to provide coated particles with good integrity of the preferred friable aminoplast polymer coatings disclosed hereinafter. While not intending to be bound by theory, it appears that the polarity of the alcohols and esters makes them especially useful with such coatings.

Moreover, the most highly preferred perfume particles of the present invention have optimal size requirements which are somewhat more stringent than various encapsulated perfumes known in the literature in order to perform optimally in laundering products of the type disclosed herein.

The present invention encompasses preferred perfume particles having an average size, when coated, of less than about 350 microns (preferably, an average size not greater than 150 microns; most preferably a size range of 100-150 microns) which comprise from about 5% to about 50% (preferably, at least about 10%) of a perfume dispersed in from about 50% to about 95% of a nonpolymeric fatty alcohol or fatty ester, or mixtures thereof, carrier material having a molecular weight of from about 100 to about 500 and a melting point of from about 37°C to about 80°C, said esters or alcohols being substantially water-insoluble, said particles having a substantially water-insoluble friable coating on their

- 11 -

outer surfaces. (By "size" herein is meant average particle diameter for substantially spherical particles, or the size of the largest diameter or dimension for nonspherical particles.) Particle sizes larger than this may be lost from the surface they are deposited on, and do not provide a relatively large enough surface area to release the perfume at the desired rate. Also, particles larger than specified herein may be undesirably noticeable on the surface being treated. Particles at the low end of the range tend to adhere well to the surface being treated, but tend to release the perfume quite rapidly. Extremely small particles outside the low end of the range tend to be rinsed off fabrics during laundering.

Typically, the particles herein are characterized by a coating which comprises up to about 30% by weight of the perfumed particles. For general use in fabric laundering and conditioning compositions, the coating typically comprises from 1% to 20%, preferably 10% to 20%, by weight of the perfumed particles.

Preferred particles herein are those wherein the friable coating is substantially water-insoluble. Suitable coatings of this type can be prepared from aminoplast polymers, e.g., the reaction products of an amine and an aldehyde. Typical friable coatings comprise, for example, the reaction products of an amine selected from urea and melamine, and an aldehyde selected from formaldehyde, acetaldehyde and glutaraldehyde, and mixtures of said amines and said aldehydes. Such friable coatings are described hereinafter.

The coated perfume particles herein are useful in situations where the particle coating is ruptured or worn away (e.g., in an automatic washing machine or laundry dryer) to release the particles, which, in turn,

- 12 -

release their perfume. Thus, the coated particles are useful in typical cleaning composition, comprising
detergent surfactants, optional builders, and the like.
The particles are likewise useful in conditioning
5 compositions, comprising fiber- and fabric-conditioning agents.

As can be seen from the foregoing and from the disclosures hereinafter, the present invention encompasses not only novel and useful perfumed particles
10 and compositions containing same, but also encompasses a method for delivering perfume-releasing particles to the surface of fabrics undergoing a laundering or softening process in a laundering apparatus, comprising adding to said laundering apparatus a detergent composition or a
15 fabric softening composition containing particles comprising the core/perfume/friable coating, as disclosed in detail herein, and operating said apparatus in standard fashion with agitation of the machine liquor and fabrics, whereupon the agitation associated with
20 said operation ruptures the coating on said particles, or fractures the particles themselves, sufficiently to allow release of the perfume when said particles become deposited onto said fabrics during said laundering or softening process.

25 Having thus described the particles prepared in the manner of this invention and their intended use and their intended use in somewhat general terms, the following describes their manufacture and use in more detail. It is to be understood that the ingredients
30 used can be any of various materials well-known in the art, and are available from various commercial sources.

The Modifier Material - The key feature of the present invention is the incorporation of various
"modifier" materials, generally of the
35 "plasticizer"-type, into the particles. Modifier materials as used herein offer several important

- 13 -

benefits. When incorporated into the perfume, a broader range of perfume materials can be accommodated in the final particles. Moreover, the modifier also appears to act as a phase transfer agent which assists in moving or retaining perfume in the core material, especially in aqueous batch processes. Importantly, it has now been determined that such materials not only reduce the undesirable batch-to-batch variation in the particles' perfume delivery performance, but also appear to enhance perfume delivery on wet fabrics, and especially on fabrics that have been treated wet (e.g., by laundering) and then dried. At present, there is no specific explanation for these latter improvements. Indeed, it is unexpected that such modifiers of the plasticizer-type would have any beneficial effect on friable coating polymers of the aminoplast type. While not intending to be limited by theory, it can be speculated that the modifier functions to modify or loosen the, presumably, lamellar structure of the friable coating (especially aminoplast coatings) such that the coating somehow loosens and allows more delivery of the perfume. Admittedly, however, the modifier materials may be functioning otherwise. Perhaps the coatings become more uniform, thus allowing for better process control. Whatever the mode of action, many materials which provide these improvements appear to fall within the class of known plasticizers.

The following are nonlimiting examples of useful modifier materials herein, and are preferably used at 0.05%, more preferably in the range from about 0.05% to about 1%, of the total particle.

1. Phthalic Acid Derivatives, bis(2-ethylhexyl)
especially Dialkyl Phthalates phthalate
diisodecyl phthalate
ditridecyl phthalate
diundecyl phthalate

- 14 -

	2. Linear Alkyl Polyesters	polyadipate (MW 6,000, Paraplex-G40)
		polyazelate (MW 2,200, Plastolein-9750)
5		polysebacate (MW 8,000, Paraplex-G25)
	3. Sebacic Acid Derivatives	di-n-butyl sebacate bis(2-ethylhexyl) sebacate
10	4. Fatty Acid Derivatives	n-butyl acetyl ricinoleate n-butyl acetoxystearate n-butyl oleate
15	5. Phosphoric Acid Derivatives	tri(2-ethylhexyl) phosphate triphenyl phosphate tricresyl phosphate
20	6. Sulfonic Acid Derivatives	N-ethyl-(o,p)- tolunesulfoamide (o,p)-tolune- sulfonamide
	7. Terephthalic Acid Derivatives	bis(2-ethylhexyl) terephthalate
25	8. Trimellitic Acid Derivatives	tris(2-ethylhexyl) trimellitate tris(heptyl, nonyl) trimellitate
30	9. Citric Acid Derivatives	tributyl citrate tributyl citrate

Of course, the modifier chosen in a given situation will depend to some extent on the odor properties of the perfume. In general, diethyl
35 phthalate is a preferred modifier.

- 15 -

The Perfume Material - In the present context, the term "perfume" means any odoriferous material or any material which acts as a malodor counteractant, i.e., deodorant. In general, such materials are characterized by a vapor pressure less than atmospheric pressure at ambient temperatures. The perfume or deodorant materials employed herein will most often be liquid at ambient temperatures, but also can be solids such as the various camphoraceous perfumes known in the art. A wide variety of chemicals are known for perfumery uses, including materials such as aldehydes, ketones, esters and the like. More commonly, naturally occurring plant and animal oils and exudates comprising complex mixtures of various chemical components are known for use as perfumes, and such materials can be used herein. The perfumes herein can be relatively simple in their composition or can comprise highly sophisticated, complex mixtures of natural and synthetic chemical components, all chosen to provide any desired odor.

Commercial grade perfumes often contain water-soluble diluents or extenders, especially glycols such as dipropylene glycol, or other diluents such as carbitol, 2-(2-ethoxyethoxy)ethyl acetate, at levels around 10-15%. There is some indication that such diluents, especially glycols such as dipropylene glycol, and the carbitols may interfere with the formation of optimal coatings, especially aminoplast coatings. While not specifically known to be critical to the practice of this invention, it is very much preferred that such diluents not be present in the perfumes at appreciable levels, i.e., above about 5%, and, most preferably, are not present in the perfume. (Water-insoluble diluents such as triethyl citrate, benzyl benzoate, and the like, can be present.) Conveniently, the potentially interfering diluent can be replaced by the water-insoluble modifier in a one-for-one substitution.

- 16 -

With regard to the perfume itself, typical perfumes herein can comprise, for example, woody/earthy bases containing exotic materials such as sandalwood oil, civet, patchouli oil and the like. The perfumes
5 herein can be of a light, floral fragrance, e.g., rose extract, violet extract and the like. The perfumes herein can be formulated to provide desirable fruity odors, e.g.,
lime, lemon, orange and the like. Suitable perfumes
10 include GLAXOLIDE, ZONALID, coumarin, heliotropin, geraniol, citronellol, and the like, or mixtures thereof.

Perfume materials such as these are described more fully in S. Arctander, Perfume Flavors and
15 Chemicals, Vols. I and II, Aurthor, Montclair, N.J., and the Merck Index, 8th Edition, Merck & Co., Inc. Rahway, N.J.

In short, any chemically compatible material which exudes a pleasant or otherwise desirable odor can
20 be used in the perfumed particles herein to provide a desirable odor when applied to fabrics.

Perfumes which are normally solid can also be employed in the present invention. These may be admixed with a liquefying agent such as a solvent prior to
25 incorporation into the particles, or may be simply melted and incorporated, as long as the perfume does not sublime or decompose upon heating.

The invention also encompasses the use of materials which act as malodor counteractants. These
30 materials, although termed "perfumes" hereinafter, may not themselves have a discernible odor but can conceal or reduce any unpleasant odors. Examples of suitable malodor counteractants are disclosed in U.S. Patent No. 3,102,101, issued August 27, 1963, to Hawley et al.

35 The perfumed particles of the present invention can even comprise perfumes which are not

- 17 -

typically used to deliver a fragrance to a surface, such as fabric through the laundry process. Perfume materials which are very volatile, unstable, or soluble in the particular compositions being used to deliver the perfume may be used in the present invention because the perfume is isolated from the composition in the particles. Perfume materials which are not substantive to fabrics in the laundry process can also be used in the present invention since the particles deliver the perfume to the fabric surface where it is released. Thus, use of the present invention to deliver a perfume to a surface broadens the class of perfume materials that can be utilized.

Generally, the perfumed particles of the present invention will comprise from about 5% to about 50%, preferably from about 20% to about 30%, perfume. The exact amount of perfume used in the particles will vary greatly depending on the strength of the particular fragrance used, and the desired odor effect.

The Core (Carrier) Material - The carrier materials which provide the core of the particles herein are characterized by several criteria which make them especially suitable in the practice of this invention. Of course, toxicologically-acceptable and non-skin irritating materials are used. As noted above, degradable materials and/or materials which are available from renewable resources are preferably used. In general, the materials are solids at room temperature and have a melting point within the range noted hereinabove. This will prevent melting of the particles in storage. (It is most desirable to have a carrier material that will not completely melt in an automatic dryer, to avoid blocking of the lint screen and excessive build-up of heat in the dryer). The melting point of the carrier material should also not be higher than a point at which the perfume to be combined

- 18 -

therewith will decompose. The melting point of the carrier material is measured by what is called the drop melting point method. American Society for Testing and Materials (ASTM) Test Method D127-63. Briefly, this method involves the following. The sample to be measured is deposited onto a thermometer bulb by dipping a chilled thermometer into the melted sample. The thermometer bearing the sample is then placed into a test tube and heated by means of a water bath until the sample melts and the first drop falls from the thermometer bulb. The average of the temperatures at which the drops of sample fall is the drop melting point of the sample.

The carrier material should also be inert to the perfume, compatible with the modifier under circumstances where the modifier is introduced into the carrier material, and relatively odorless. The carrier material must allow for diffusion of the perfume therethrough. The carrier material must also be such that it melts without decomposition.

Having thus described the carrier materials useful herein with regard to their physico-chemical properties, the following illustrates various nonpolymeric compounds which can be used as carrier materials herein.

One class of carrier materials which is highly preferred herein comprises the fatty alcohols. The fatty alcohols of chain length of at least C_{14} are substantially water-insoluble. Substantial water-insolubility is an important feature of the carrier materials in-use, since if the particle dissolves, e.g., in a laundering liquid, it releases its perfume immediately and thus does not deposit onto fabrics to provide the intended prolonged release of said perfume. Accordingly, by "substantially water-insoluble" herein is meant that the carrier materials

- 19 -

will not be dissolved in water to an extent greater than about 10%, preferably not greater than 5%, by weight, at the temperatures of the aqueous media in which they are used.

5 Moreover, fatty alcohols are typically solid at room temperature, i.e., they have a melting point above about 30°C, and typically will melt over the range of about 37°C to about 75°C. The most highly preferred carrier materials of this class will be selected from
10 molecules which will not undesirably interact with the perfumes which they are carrying, nor have a substantial amount of undesirable odor characteristics of their own. For example, the preferred alcohol carriers described hereinafter will, in general, preferably not be
15 contaminated with lower molecular weight alcohols or fatty acids which could result in "goaty" or rancid odors, unless, of course, such odors are a desired complement to the perfume being carried. In particular, the straight-chain fatty alcohols are preferred, since
20 they are available from natural sources. However, branched-chain and some unsaturated alcohols may also be used.

 Among the fatty alcohol class of carriers, those in the C₁₄-C₁₈ chain length are most preferred.
25 For reasons of possible malodor, as noted above, it is generally preferred that the alcohols be substantially free of C₄-C₁₀ chain-length alcohols and their fatty acid oxidation products. More specifically, n-C₁₄OH (myristyl alcohol/tetradecanol) is preferred under lower
30 temperature laundering conditions in the United States, whereas C₁₆-C₁₈ alcohols can be used under the somewhat higher temperature laundering conditions found in some European countries. Higher alcohols are also desirable where a long-lasting perfume benefit is desired. C₁₂
35 alcohols can also be present in the cores. However, it will be appreciated that cores containing substantial

- 20 -

amounts of C₁₂ alcohols may liquefy under some warehouse storage conditions, and the resulting liquid core/coated particles are more fragile than solid core/coated particles, and are subject to fracture when the product is shipped. The C₂₀-C₂₄ alcohols are also useful under some conditions, although these latter materials are in considerably shorter supply than the C₁₄-C₁₈ materials and are, consequently, more expensive. Mixtures of the fatty alcohols may also be used, provided that they meet the above-noted criteria.

In addition to the alcohols noted hereinabove, the following are representative, nonlimiting examples of alcohols which can be used as the core materials herein: n-pentadecanol, n-hexadecanol, n-heptadecanol, n-octadecanol, n-docosanol, n-heneicosanol, 16-methylheptadecanol, 26-methylheneicosanol, 22-methylpentacosanol, and 18-methyleicosanol.

Other nonlimiting examples of nonpolymeric carrier materials useful herein include various esters having melting points of at least about 30°C, preferably from about 37°C to about 75°C. The same considerations regarding substantial water-insolubility, acceptable odor characteristics, etc., noted for the alcohols are also important factors to be considered with the ester perfume carrier materials.

In general, the esters will comprise at least about 18 carbon atoms. Suitable esters include, for example, lower (typically C₁-C₄) alkyl esters of fatty acids which, chemically, comprise fatty acid esters of lower monohydric alcohols. Likewise, various fatty acid esters of polyhydric alcohols can be employed herein, as long as the water-insolubility parameter is met. Fatty acid triglycerides, e.g., "fats", meeting the foregoing parameters are also suitable for use herein, assuming proper deodorization.

- 21 -

The following examples of suitable ester carrier materials are given by way of illustration, and not by way of limitation. It will be appreciated by those skilled in the art that such esters are commercially available from various sources. Such esters include: methyl stearate; ethyl stearate; methyl nona-decylate; ethyl nonadecylate; methyl arachidate; methyl behenate; the monostearyl and monopalmityl esters of ethylene glycol; the monostearyl and monopalmityl esters of propylene glycol; the monostearyl and monopalmityl esters of trimethylene glycol. Various diesters of the foregoing polyols can also be used, based on their melting points and solubility characteristics.

In a less preferred, but useful, mode the carrier materials can be polymeric. Solid polymeric carrier materials must also meet certain criteria to be useful in the present invention. First, the carrier material must be a water-insoluble polymeric material. Further, the material must have a molecular weight between about 100 and about 30,000, preferably between about 500 and about 5000. The molecular weight of the carrier material may be determined by any standard means. The material must also have a melting point of between about 37°C and about 190°C, typically 37°C to 130°C. This will prevent melting of the particles in storage or the washing machine in laundry applications. (It is most desirable to have a carrier material that will not completely melt in an automatic dryer, to avoid blocking of the lint screen and excessive build-up of heat in the dryer). The melting point of the carrier material should also not be higher than a point at which the perfume to be combined therewith will decompose. The melting point of the carrier material is measured by what is called the drop melting point method. American Society for Testing and Materials (ASTM) Test Method

- 22 -

D127-63. Briefly, this method involves the following. The sample to be measured is deposited onto a thermometer bulb by dipping a chilled thermometer into the melted sample. The thermometer bearing the sample
5 is then placed into a test tube and heated by means of a water bath until the sample melts and the first drop falls from the thermometer bulb. The average of the temperatures at which the drops of sample fall is the drop melting point of the sample.

10 The polymeric carrier material must also be of a particular hardness. This hardness value may be measured by the standard test method for needle penetration of petroleum waxes. ASTM Test Method D1321-86. Briefly, this method involves first melting
15 and further heating the sample to be tested to 17°C (30°F) above its congealing point. The sample is then poured into a container and air cooled under controlled conditions. The sample is then conditioned at the test temperature in a water bath. Penetration is then
20 measured with a penetrometer, which applies a standard needle to the sample for five seconds under a load of 100 grams. The penetration or hardness value is the depth, in tenths of a millimeter, to which the standard needle penetrates into the wax under these defined
25 conditions. The hardness value of the carrier material must be between about 0.1 and about 15, preferably between 0.1 and 8, to be useful in the present invention. This will allow for particles of a hardness that will optimize the perfume protection/preservation
30 in the carrier.

The polymeric carrier material must also be inert to the perfume and relatively odorless. The material must allow for diffusion of the perfume therethrough. The carrier material must also be such
35 that it melts without decomposition.

- 23 -

Nonlimiting examples of useful polymeric carrier materials include polyethylenes, polyamides, polystyrenes, polyisoprenes, polycarbonates, polyesters, polyacrylates, vinyl polymers and polyurethanes and mixtures thereof, which meet the above-described criteria, e.g., they are water-insoluble, have a molecular weight between about 100 and about 30,000, have a melting point between about 37°C and 190°C and a hardness value between 0.1 and 15.

Highly preferred polymeric carriers will have a hardness value of 0.1 to 8, typically 0.5; a molecular weight of 500 to 5,000 (typically 2,000); and a melting point of about 126°C typically, a polyethylene.

One polymeric carrier material which meets all of these specified criteria is sold under the trade name POLYWAX 2000 by Petrolite Specialty Polymers Group. This material is a polyethylene having a molecular weight of about 2,000, a melting point of about 259°F (126°C), and a hardness value (as measured above) at 77°F (25°C) of about 0.5. Another material which meets these criteria is POLYWAX 1000 (also sold by Petrolite Specialty Polymers Group). This material is also a polyethylene having a molecular weight of about 1,000, a melting point of about 237°F (114°C), and has a hardness value at 77°F (25°C) of about 1.0. Another such material is POLYWAX 500.

It may be desirable to utilize a mixture of different polymeric carrier materials in the perfume particles of the present invention, for example, a blend of a polymeric material and a minor amount of a wax material. Examples of useful wax materials include the materials sold under the trade names BOLER 1014, STARWAX 100, and VICTORY, all available from the Boler Petroleum Company. Such a blend allows for better deposition properties because the particles formed therefrom would have a "stickier" surface. A great number of

- 24 -

combinations of materials are possible and are intended to be covered by this invention so long as the final blend of carrier materials meets the criteria outlined above.

5 The choice of polymeric carrier material to be used in the perfumed particles of the present invention will depend to some degree on the particular perfume to be used. Some perfumes will require a greater amount of protection than others and the carrier material to be
10 used therewith can be chosen accordingly.

 Generally, the perfumed particles used in the present invention will comprise from about 30% to about 95%, preferably from about 50% to about 95% polymeric carrier material. Again, this will vary with the type
15 and amount of the particular perfume being utilized.

 In a typical process, the core of the perfume-containing particles can be perfumed as follows. The carrier material is first heated slowly to its melting point. The material is not heated any more than is
20 necessary to just melt the substance. The perfume is then quickly added, generally as an oil or liquid, at room temperature to the melted carrier substance. The two are quickly mixed into a homogeneous blend then rapidly cooled with liquid nitrogen (or with dry ice or
25 any other means which will cool the mixture quickly) until it has completely solidified. The solid material is then subdivided, generally by grinding or methods such as spray cooling or extrusion may also be used to subdivide the particles.

30 To further stabilize particularly volatile or delicate perfumes, it may be desirable to preload the perfume (i.e., mix the perfume) onto silica gel or clay prior to combining with the carrier material. Some perfumes which are not so volatile will not require this
35 special treatment because it would inhibit their release from the carrier material too much. Optimization of the

- 25 -

rate at which the perfume is released from the carrier is the goal, and this optional additional step allows for better control of that rate with some of the more volatile perfumes.

5 The Coating Material - The perfume-containing particles, above, are encapsulated to provide a friable coating. This coating prevents the perfume from diffusing out of the particles as readily during long storage periods. Moreover, the coating helps preserve the
10 original "character" of perfumes having particularly volatile top-notes. Moreover, the coating helps protect the perfumed particle from other ingredients in the formulation being perfumed.

 The coating materials used herein are friable,
15 and are designed to break-up as the perfumed formulation is used, thereby releasing the perfumed particle.

 The particles may be coated with more than one friable coating material to produce a particle having more than one layer of coating. Alternatively,
20 different particles can have a distribution of different coating thicknesses to allow a range of perfume release times. Different coating materials can be chosen to provide different perfume protection as needed, so long as one of the coatings, generally, the outermost, is
25 friable.

 The individual perfume-containing particles may also be agglomerated with the coating material to provide larger particles which comprise a number of the individual perfume-containing particles. This
30 agglomerating material surrounding the particles provides an additional barrier to diffusion of the perfume out of the particles. Such an approach also minimizes the surface area of free particles susceptible to perfume diffusion. The ratio of perfume particles to
35 agglomerate material will vary greatly depending upon the extent of additional protection desired. This

- 26 -

agglomeration approach may be particularly useful with very volatile perfumes or perfumes that are especially susceptible to degradation. Also, agglomeration of very small perfume particles would provide additional protection against premature diffusion out of perfume.

Agglomeration of particles in this fashion is useful in preventing segregation of small perfume particles from larger detergent granules, for example, in a dry granular detergent product.

Process of Manufacture -

(a) Incorporation of Modifier: In a preferred method for preparing the particles of the present invention, the modifier is introduced into the system as a component of the perfume material. Typically, the modifier comprises at least about 1% by weight of the perfume, and more typically comprises from about 1% to about 50%, more preferably about 10% to about 20%, by weight of the perfume material. Also as noted above, in a preferred method the perfume ingredient is substantially free of diluent such as dipropylene glycol. In point of fact, commercial perfumes often contain dipropylene glycol, so it is a simple matter to substitute a modifier such as diethyl phthalate for the dipropylene glycol typically present in commercial perfume compositions.

In an alternate mode, rather than adding the modifier to the perfume, the modifier is admixed with the carrier core material, i.e., material such as myristyl alcohol or polyethylene mentioned hereinabove. The perfume is then added. In such method of addition, the modifier will typically comprise from about 1% to about 15% by weight of the core material.

In still another, but less preferred, mode the modifier can be added directly to the friable coating material. In one method of operation, the perfume/solid core is prepared and enrobed in the friable coating.

- 27 -

Thereafter, while the coating is still relatively fresh, a small amount of modifier (e.g., about 0.05% by weight of the total coating used) can be sprayed onto the coating. The final particle, with spray-on modifier, can then be cured at temperatures of around 120°F for a period of a few hours in order to desirably plasticize the coating. It will be appreciated by the formulator, however, that this means of adding the modifier to the particles is somewhat more difficult than simply adding the modifier to the perfume or, less preferably, to the carrier, as noted hereinabove.

(b) Coating: For friable coatings, the process of manufacture is based on applying the coating as a kind of "shell" to the perfumed particles. For perfumed particles whose carrier material has a melting point below that of the boiling point of the solvent used in the process, the process involves adding the carrier and perfume to a solution of the "shell" material, or a suitable precursor, held above the carrier melting temperature. The system is agitated sufficiently to form an emulsion of the carrier/perfume of desired liquid drop size in the shell solution. The conditions necessary to deposit the encapsulating material are then established and the whole is cooled to give encapsulated solid particles having the desired, friable "shell". Water insolubility of the shell is established either at the deposition stage, or by suitable treatment prior to isolation or use of the particles.

Although the process described here is a one step molten drop formation/encapsulation procedure, it should be readily apparent to those skilled in the art that encapsulation of preformed perfume particles can be accomplished in a like manner. The preformed particles can be prepared in a variety of ways, including cryogrinding, spray drying, spray congealing and

- 28 -

meltable dispersion techniques such as those described in books by P. B. Deasy ("Microencapsulation & Related Drug Processes", Dekker, N.Y., 1986) and A. Kondo ("Microcapsule Processing and Technology", Dekker, N.Y., 1979). Such techniques would be required for carrier materials having a melting point above the solvent boiling point. A variety of suitable encapsulation procedures can be used, such as reviewed in the books by Deasy and Kondo above. Depending on materials used, the shell can impart hydrophilicity or hydro-phobicity to the particles. For examples of encapsulating materials and processes including gelatin-gum arabic concentrate deposited by a complex coacervation procedure, see, e.g., U.S. Patent 2,800,457, and urea-formaldehyde deposited by a polycondensation process, e.g., U.S. Patent 3,516,941. Water insolubility of shell materials may be imparted, for example, by cross-linking of gelatin-gum arabic coacervate with suitable aldehydes or other known gelatin hardeners after deposition. Polymerization of the urea-formaldehyde precondensate during an encapsulation process inherently yields water-insolubility.

The slurry containing the perfume particles can be used directly, e.g., admixed and dried with other components of the granular detergent formulations, or the particles can be washed and separated, and dried if desired.

EXAMPLE I

Perfume particles containing a hydrophobic, water-insoluble, friable coating deposited by polycondensation are prepared as follows.

A urea-formaldehyde precondensate is first formed by heating a mixture of 162 g 37% aqueous formaldehyde and 60-65 g urea, adjusted to pH 8.0 with

- 29 -

0.53 g sodium tetraborate, for 1 hour at 70°C, and then adding 276.85 g water.

429 ml of this precondensate and 142 ml water are then stirred in a 1-1 steel reactor and 57.14 g sodium chloride and 0.57 g sodium carboxymethyl cellulose added. Then are added the core components comprising 166.2 g C₁₄H₂₉OH carrier and 55.8 g perfume, said perfume comprising 11.8% by weight of diethyl phthalate and being substantially free of dipropylene glycol, and the reactor is heated to about 90°C. Agitation is adjusted to emulsify and maintain the molten core at the desired drop size, and the pH of the contents is adjusted to about 5.0 with dilute hydrochloric acid.

The reactor is then allowed to cool to room temperature with a gradual pH reduction to 2.2 over a 2 hour period. The reactor is then increased to about 50°C for a further 2 hours, then cooled to room temperature, after which the pH is adjusted to 7.0 with 15% ammonium hydroxide solution.

The resultant slurry containing the solid core particles encapsulated with urea-formaldehyde polymer may be used directly, or may be isolated by separation, washing and air drying as required.

Compositions - The coated perfumed particles prepared in the foregoing manner can be used in all types of products where it is desirable to deposit fragrances on treated surfaces, and wherein sufficient agitation or pressure is exerted to rupture the friable coating. Typical examples of such products are laundry detergents and fabric softeners. The following illustrates the use of the compositions of this invention in such products.

Laundry cleaning products comprise: a
detergent surfactant (typically 5%-30% wt.); optionally but typically, one or more detergency builders (10%-55%

- 30 -

wt.); optionally, 3%-20% wt. of various enzymes, bleaches, carriers, and the like, all well-known from standard texts and very familiar to detergent formulators. Surfactants include soap, alkyl benzene sulfonates, ethoxylated alcohols, alkyl sulfates, 5 alpha-sulfonated fatty acids, and the like. Builders include various phosphates, zeolites, polycarboxylates and the like. U.S. Patents 3,985,669, 4,379,080 and 4,605,609 can be referred to for typical listings of 10 such ingredients.

Modern fabric softeners typically comprise about 3%-35% wt. of one or more fabric softening compounds, such as quaternary ammonium salts, e.g., ditallowdimethyl ammonium chloride or imidazoline or 15 imidazolinium compounds. Softeners (and antistatic agent) generally have one, or preferably two, C₁₂-C₁₈ alkyl substituents and two or three short chain alkyl groups. Again, such materials are conventional and well-known to softener formulators.

20 It is to be understood that one of the major advantages of the coated perfumed particles of this invention is their ability to be stably formulated (typically 0.1%-10% wt.) in combination with conventional detergent, bleach and fabric treatment 25 compositions without difficulty.

EXAMPLE II

A granular laundry detergent is as follows:

- 31 -

	<u>Component</u>	<u>Weight %</u>
	Sodium C ₁₃ alkylbenzene sulfonate	7.5
	Sodium C ₁₄₋₁₅ alkylsulfate	7.5
	C ₁₂₋₁₃ alkyl polyethoxylate (6.5) stripped of	
5	unethoxylated alcohol and lower ethoxylate	2.0
	C ₁₂ alkyltrimethyl ammonium chloride	1.0
	Sodium tripolyphosphate	32.0
	Sodium carbonate	10.0
	Sodium perborate monohydrate	5.3
10	Sodium octanoyloxybenzene sulfonate	5.8
	Sodium diethylene triamine pentaacetate	0.5
	Sodium sulfate, H ₂ O and minors	Balance

The above composition is prepared using conventional means. The composition is combined with the perfume particles of Example I as follows. An amount of the perfume particles of Example I is simply dry-blended with the detergent composition so that the detergent composition comprises about 0.3% perfume.

The particles may be simply mixed in with the detergent granules. To prevent segregation of the perfume particles during packaging and shipping (due to their smaller size relative to the detergent granules), the particles can optionally be coated or agglomerated with a water-soluble coating material (on top of the friable coating) prior to combining with the detergent granules. This can be accomplished with a Schugi mixer (Flexomix 160) where a sufficient amount of a dextrin glue solution (2% dextrin, 3% water) is sprayed onto the particles to result in agglomerates of perfume particles in the same size range as other detergent granules.

The perfume is protected in the particles from degradation by the bleach in the detergent composition over long periods of storage. When used in the laundry process in an automatic washing machine this detergent composition will provide perfume fragrance in

- 32 -

substantially its original state from product, through the wash process and onto the fabric.

A great number of perfumes can be utilized in the present composition that would not otherwise be appropriate for use in such laundry detergent compositions.

EXAMPLE III

A liquid fabric softener for use in an aqueous laundry rinse bath is as follows:

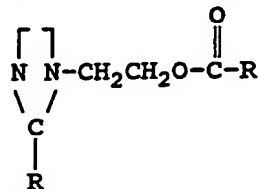
<u>Component</u>	<u>Weight %</u>
Softener A*	3.00
Softener B**	5.00
HCl	0.29
Polydimethylsiloxane	0.15
Polyethylene Glycol (4000)	0.30
Bronopol (Antimicrobial)	100 ppm
Calcium Chloride	30 ppm
Dye	30 ppm
Coated Perfume Particles***	4.0
Water	Balance

*Softener A is



wherein each R group is in the C₁₅-C₁₈ alkyl range.

**Softener B is



wherein each R group is in the C₁₅-C₁₈ alkyl range.

***Particles prepared according to Example I. 80-100 micron size range; 20% coating weight.

When used in the rinse bath of an automatic washing machine, the coating on perfumed particles of Example III is ruptured and the particles provide a fragrance to the fabrics being treated.

- 33 -

EXAMPLE IV

A liquid laundry detergent composition is as follows:

	<u>Component</u>	<u>Weight %</u>
5	C ₁₃ linear alkylbenzene sulfonic acid	7.2
	C ₁₄₋₁₅ alkyl polyethoxylate (2.25)	
	sulfuric acid	10.8
	C ₁₂₋₁₃ alcohol polyethoxylate (6.5)*	6.5
	C ₁₂ alkyl trimethylammonium chloride	1.2
10	C ₁₂₋₁₄ fatty acid	13.0
	Oleic acid	2.0
	Citric acid (anhydrous)	4.0
	Diethylenetriamine pentaacetic acid	0.23
	Protease enzyme (2.0 AU/g)	0.75
15	Amylase enzyme (375 Am. U/g)	0.16
	TEPA-E,5-18**	1.5
	Monoethanolamine	2.0
	(moles of alkanolamine)	(0.033)
	Sodium ion	1.66
20	Potassium ion	2.65
	(molar K+:Na+)	(0.94)
	Propylene glycol	6.8
	Ethanol	7.8
	Formic acid	0.66
25	Calcium ion	0.03
	Minors and water	Balance to 100
	pH at concentration of 10%	
	in water at 68°F (20°C)	8.65

*Alcohol and monoethoxylated alcohol removed.

- 30 **Tetraethylene pentaamine ethoxylated with 15-18 moles (avg.) of ethylene oxide at each hydrogen site.

The detergent is prepared by adding the components, with continuous mixing, in the following order: paste premix of alkylbenzene sulfonic acid,

- 35 sodium hydroxide, propylene glycol and ethanol; paste premix of alkyl polyethoxylate sulfuric acid, sodium

- 34 -

hydroxide and ethanol; pentaacetic acid; alcohol polyethoxylate; premix of water, brighteners, alkanolamine and alcohol polyethoxylate; ethanol; sodium and potassium hydroxide; fatty acid; citric acid; formic acid and calcium; alkyl trimethylammonium chloride; TEPA-E₁₅₋₁₈; adjust pH to about 8.1; and balance of components.

The above composition is combined with the perfume-containing particles prepared according to Example I as follows. An amount of the perfume particles of Example I (avg. size range 40-150 microns; 5% coating) is thoroughly mixed into the liquid detergent composition so that the detergent composition comprises about 0.3% perfume (about 1% of the detergent composition will comprise the perfume particles).

EXAMPLE V

A fiber- and fabric-softener composition is as follows:

<u>Component</u>	<u>Weight%</u>
Softener C*	3.7
TAMET**	0.3
GMS***	1.20
Phosphoric Acid	0.023
Polydimethylsiloxane (350)	0.10
Glutaraldehyde	550 ppm
Blue Dye	10 ppm
Coated Perfume Particles****	3.0
*(R ¹) ₂ (CH ₃) ₂ N ⁺ , Br ⁻ , wherein R ¹ is mixed C ₁₂ -C ₁₈ alkyl (i.e., "tallowalkyl").	

**TAMET is tallowalkyl N(CH₂CH₂OH)₂.

***GMS is glyceryl monostearate.

****Coated perfume particles per Example I, sieved to average size less than 100 microns. Coating weight 20%.

It will be appreciated by those skilled in the art that the anions, X, used with any of the cationic

- 35 -

fabric softeners herein are a routine matter of choice, and that X can be, for example, chloride, bromide, methylsulfate, and the like. Mixtures of fabric softeners can be used, as can mixtures of anions.

5

EXAMPLE VI

The fabric softener composition of Example III is modified by using perfumed particles with friable coatings (melamine/urea/formaldehyde; 0.1/1/1.1 mole ratio; 80 micron size) with coating weights of about 20%, respectively. It is to be noted that melamine substitution for about 15% of the urea in the aminoplast coatings is preferred for use in fabric softeners. It is also to be noted that particles above about 80 microns are visible in softener products.

10

15

EXAMPLE VII

A deterative bar composition is prepared by gently (so as not to fracture the coating) admixing 2% by weight of the coated perfumed particles of Example I (7% coating; all particles through 150 micron sieve) into a 99.44% tallow soap mixture (Na salt) and formed into a bar in a pin die. The compositions herein can also be used in combination with abrasives. As is well-known, abrasive cleaners typically comprise 10% to 90+% abrasive such as pumice, silica, calcium carbonate, and the like. Coated perfume particles used in such cleaners are ruptured, in-use, to release their perfume.

20

25

30

EXAMPLE VIII

An abrasive cleanser is as follows:

- 36 -

	<u>Component</u>	<u>Weight %</u>
	Sodium tallow sulfate	1.0
	Calcium carbonate	40.0
	Pumice (through 60 micron sieve)	45.0
5	Sodium sulfate	10.0
	Coated perfume particles*	3.0
	Chlorinated trisodium phosphate	1.0
	*Per Example I; 10% coating; particles through 100 micron sieve.	

10 The composition of Example VIII is prepared by gently dry-blending the ingredients.

 It will be appreciated by the formulator that the weight (or thickness) of operable friable coatings can be adjusted according to the usage envisioned. For
15 example, even relatively thick coatings will rupture and release their perfume particles under European machine washing conditions, which can involve wash times of many minutes, at high temperature and considerable agitation. By contrast, USA machine washing conditions are much
20 shorter, and milder, so less coating material should be used. For fabric softeners, agitation and agitation times are usually less than for washing.

EXAMPLE IX

25 A bleach composition comprises ca. 6% aqueous hypochlorite/H₂O containing 10% (wt.) of the particles of Example I. The product is shaken prior to use as a clothes bleach or toilet bowl disinfectant to suspend the particles.

30

- 37 -

EXAMPLE X

A granular laundry detergent is as follows:

	<u>Component</u>	<u>Weight %</u>
	C ₁₂ alkylbenzene sulfonate	5.64
5	Tallow alcohol sulfate	2.42
	Sodium sulfate	22.00
	Sodium silicate	8.00
	Magnesium sulfate	0.40
	Carboxymethyl cellulose	0.29
10	EDTA	0.29
	Brightener 47	0.15
	Sodium tripolyphosphate	21.34
	C ₁₄₋₁₅ E07 surfactant*	5.00
	Sodium perborate 4H ₂ O	13.23
15	Sodium perborate 1H ₂	1.96
	Sodium carbonate	7.00
	Proteolytic enzyme	0.79
	TAED**	3.03
	Perfume particles***	1.00
20	Water/minors	Balance
	*As Dobanol 45-7	
	**Tetraacetylenethylenediamine	
	***Prepared per Example I; 100-150 micron size; 20% coating.	

25



- 38 -

EXAMPLE XI

A concentrated detergent granule is as

follows:

	<u>Component</u>	<u>Weight %</u>
5	Sodium linear alkyl benzene sulfonate with an average chain length of 12.4	13.9
	Sodium alkylsulfate with an average chain length of 14.5	5.9
	Aluminosilicate (Zeolite A; 1-10 micron)	25.36
10	Polyacrylate 4500	4.47
	Polyethylene glycol 8000	1.46
	Sodium carbonate	17.82
	Sodium sulfate	11.06
	Silicate solids	2.05
15	Brightener	150.29
	Moisture	7.70
	Miscellaneous	0.57
	Enzyme	0.78
	Nonionic - C ₁₂₋₁₃ EO _{6.5}	1.07
20	Citric acid	6.57
	Perfume particles*	1.00
	*Per Example I; 100-150 micron size	

The foregoing Examples illustrate the practice of this invention using nonpolymeric core materials.

- 25 The following illustrates the use of a polymeric core material. In the following Examples, the perfume is modified by the addition of modifier in the manner disclosed hereinabove.

30 EXAMPLE XII

Perfume particles containing a hydrophobic, water-insoluble coating deposited by polycondensation are prepared as follows:

- 35 A urea-formaldehyde precondensate is first formed by heating a mixture of 162 g 37% aqueous formaldehyde and 60-65 g urea, adjusted to pH 8.0 with

- 39 -

0.53 g sodium tetraborate, for 1 hour at 70°C, and then adding 276.85 g water.

- 429 ml of this precondensate and 142 ml water are then stirred in a 1-1 steel reactor and 57.14 g sodium chloride and 0.57 g sodium carboxymethyl cellulose added. Then are added the core components comprising 161.3 g POLYWAX 500 carrier and 60.7 ml perfume, said perfume containing 15% by weight of diethyl phthalate and being substantially free of dipropylene glycol, and the reactor is heated to about 10°C above the core melting point. Agitation is adjusted to emulsify and maintain the molten core at the desired drop size, and the pH of the contents is adjusted to about 5.0 with dilute hydrochloric acid.
- The reactor is then allowed to cool to room temperature with a gradual pH reduction to 2.2 over a 2 hour period. The reactor is then increased to about 50°C for a further 2 hours, then cooled to room temperature, after which the pH is adjusted to 7.0 with 10% sodium hydroxide solution. The resultant slurry containing the solid core particles encapsulated with urea-formaldehyde polymer may be used directly, or may be isolated by separation, washing and air drying as required. The coated perfumed particles prepared in the foregoing manner can be used in all types of products where it is desirable to deposit fragrances on treated surfaces, and wherein sufficient agitation or pressure is exerted to rupture the friable coating. Typical examples of such products are laundry detergents and fabric softeners.
- The following illustrates the use of the compositions of this invention in such products.

- 40 -

EXAMPLE XIII

A granular laundry detergent is as follows:

	<u>Component</u>	<u>Weight %</u>
	Sodium C ₁₃ alkylbenzene sulfonate	7.5
5	Sodium C ₁₄₋₁₅ alkylsulfate	7.5
	C ₁₂₋₁₃ alkyl polyethoxylate (6.5) stripped of unethoxylated alcohol and lower ethoxylate	2.0
	C ₁₂ alkyltrimethyl ammonium chloride	1.0
10	Sodium tripolyphosphate	32.0
	Sodium carbonate	10.0
	Sodium perborate monohydrate	5.3
	Sodium octanoyloxybenzene sulfonate	5.8
	Sodium diethylene triamine pentaacetate	0.5
15	Sodium sulfate, H ₂ O and minors	Balance

The above composition is prepared using conventional means. The composition is simply dry-blended with an amount of the 10 perfume particles of Example XII so that the detergent composition comprises about 0.3% perfume.

- 41 -

WHAT IS CLAIMED IS:

1. In a method for preparing a particulate perfume delivery system comprising a solid core material bearing a perfume material and having a friable coating
5 surrounding said perfume-bearing core material, comprising the steps of combining said core with said perfume and encapsulating said perfumed core with a friable polymeric coating, the improvement which comprises introducing a modifier material into said
10 perfume delivery system.
2. A method according to Claim 1 wherein said modifier material is introduced as a component of said perfume material.
15
3. A method according to Claim 2 wherein said modifier material is a phthalate-type modifier.
4. A method according to Claim 2 wherein said modifier
20 material is diethyl phthalate.
5. A method according to Claim 4 wherein said perfume material is substantially free of dipropylene glycol.
- 25 6. A method according to Claim 1 wherein the friable coating is an aminoplast polymer.
7. A method according to Claim 6 wherein said aminoplast polymer is the reaction product of an amine
30 selected from urea and melamine, or mixtures thereof, and the aldehyde is selected from formaldehyde, acetaldehyde, glutaraldehyde, or mixtures thereof.
8. A method according to Claim 7 wherein said
35 aminoplast polymer is urea-formaldehyde polymer.

- 42 -

9. A method according to Claim 1 wherein said modifier material is introduced as a component of said core material.
- 5 10. A method according to Claim 9 wherein said modifier material is a phthalate-type modifier.
11. A method according to Claim 10 wherein said modifier material is diethyl phthalate.
- 10 12. A method according to Claim 1 wherein said modifier material is introduced as a component of said friable coating material.
- 15 13. A method according to Claim 12 wherein said modifier material is a phthalate-type modifier.
14. A method according to Claim 13 wherein said modifier material is diethyl phthalate.
- 20 15. A perfume delivery system, comprising: coated perfume particles having an average size, when coated, of less than about 350 microns which comprise from about 5% to about 50% by weight of a perfume dispersed in from
25 about 50% to about 95% by weight of a nonpolymeric solid fatty alcohol or fatty ester carrier material, or mixtures thereof, said alcohols or esters having a molecular weight of from about 100 to about 500 and a melting point of from about 37°C to about 80°C, said
30 alcohols or esters being substantially water-insoluble, said particles having a substantially water-insoluble friable coating on their outer surfaces, said particles containing at least about 0.05% by weight of a modifier.
- 35 16. The particles according to Claim 15 which have an average size not greater than 150 microns.

- 43 -

17. The particles according to Claim 15 wherein said modifier material is a phthalate-type modifier.

18. The particles according to Claim 17 wherein said
5 modifier material is diethyl phthalate.

19. The particles according to Claim 18 wherein said perfume material is substantially free of dipropylene glycol.

10

20. The particles according to Claim 15 wherein the friable coating is an aminoplast resin.

21. The particles according to Claim 20 wherein the
15 coating comprises the reaction product of an amine selected from urea and melamine, and an aldehyde selected from formaldehyde, acetaldehyde and glutaraldehyde, and mixtures of said amines and said 5 aldehydes.

20

22. The particles according to Claim 15 wherein said modifier material is introduced as a component of said perfume material.

23. The particles according to Claim 15 wherein the
25 carrier material comprises an alcohol selected from the C₁₄-C₁₈ alcohols.

24. A detergent composition, comprising one or more
30 deterative surfactants, optionally, one or more builders, and a perfume delivery system comprising perfume particles which comprise from about 5% to about 50% by weight of a perfume dispersed in from about 50% to about 95% by weight of a nonpolymeric solid fatty alcohol or
35 fatty ester carrier material, or mixtures thereof, said alcohols or esters having a molecular weight of from

- 44 -

about 100 to about 500 and a melting point of from about 37°C to about 80°C, said alcohols or esters being substantially water-insoluble, said particles having a substantially water-insoluble friable coating on their outer surfaces, said coated particles having an average size less than about 350 microns, said particles containing at least about 0.05% by weight of a modifier.

25. A perfume delivery system, comprising: coated perfume particles having an average size, when coated, of less than about 350 microns which comprise from about 5% to about 70% of a perfume dispersed in from about 30% to about 95% of a water-insoluble polymeric carrier material having a molecular weight of from about 100 to about 30,000, a melting point of from about 37°C to about 190°C, and a hardness value of from about 0.1 to about 15, said particles having a friable coating on their outer surfaces, said particles containing at least about 0.05% by weight of a modifier.

20

26. The particles according to Claim 25 which have an average size not greater than 150 microns.

27. The particles according to Claim 26 wherein the modifier is a phthalate-type modifier.

25

28. The particles according to Claim 27 wherein the modifier is diethyl phthalate.

29. The particles according to Claim 25 wherein the coating comprises the reaction product of an amine selected from urea and melamine, and an aldehyde selected from formaldehyde, acetaldehyde and glutaraldehyde, and mixtures of said amines and said aldehydes.

30
35

- 45 -

30. The particles according to Claim 25 wherein the carrier material comprises polyethylene.

5 31. A detergent composition, comprising one or more
detergent surfactants, optionally, one or more builders,
and perfume particles which comprise from about 5% to
about 70% of a perfume dispersed in from about 30% to
about 95% of a water-insoluble polymeric carrier
10 material having a molecular weight of from about 100 to
about 30,000, a melting point of from about 37°C to
about 190°C, and a hardness value of from about 0.1 to
about 15, said particles having a friable coating on
their outer surfaces, said coated particles having an
average size less than about 350 microns, said particles
15 containing at least about 0.05% by weight of a modifier.

32. A fabric softener composition comprising a fabric softener compound and the particles of Claim 15.

20 33. A fabric softener composition comprising a fabric softener compound and the particles of Claim 25.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/03156

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C11D3/50; C11D17/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C11D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP,A,0 397 245 (PROCTER & GAMBLE) 14 November 1990 see claims 1,6,7,9-14; examples ---	1-8, 12-15, 25-31,33
Y	EP,A,0 397 246 (PROCTER & GAMBLE) 14 November 1990 see claims 1-10,11-27; examples & US,P,89 350 434 (PROCTER & GAMBLE) 11 May 1989 cited in the application ---	1-8, 12-15, 25-31,33
A	FR,A,2 333 041 (PROCTER & GAMBLE) 24 June 1977 & US,A,4 145 184 20 March 1979 cited in the application see claims; examples --- -/-	1,5-8, 24,25,31
<p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
08 SEPTEMBER 1992	11. 09. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	GRITTERN A.G.	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9203156
SA 60442**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 08/09/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0397245	14-11-90	AU-A- 5491290	29-11-90
		CA-A- 2015736	11-11-90
		CN-A- 1047336	28-11-90
		JP-A- 3033196	13-02-91

EP-A-0397246	14-11-90	AU-A- 5491690	15-11-90
		CA-A- 2015737	11-11-90
		CN-A- 1047335	28-11-90
		JP-A- 3041197	21-02-91

US-P-89350434		None	

FR-A-2333041	24-06-77	US-A- 4145184	20-03-79
		BE-A- 848831	26-05-77
		CA-A- 1081078	08-07-80
		DE-A- 2653329	02-06-77
		GB-A- 1560640	06-02-80
		JP-A- 52086411	18-07-77
		NL-A- 7613204	01-06-77

US-A-4145184	20-03-79	BE-A- 848831	26-05-77
		CA-A- 1081078	08-07-80
		DE-A- 2653329	02-06-77
		FR-A, B 2333041	24-06-77
		GB-A- 1560640	06-02-80
		JP-A- 52086411	18-07-77
		NL-A- 7613204	01-06-77

US-A-4842761	27-06-89	EP-A- 0334490	27-09-89

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,4 842 761 (H.J. RUTHERFORD) 27 June 1989 see claims 1-7 ---	15,24, 25,31

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☒ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☒ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.